Materials Science and Engineering A 532 (2012) 354–361

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Effect of nano-SiO_2 and nano-TiO_2 addition on the rheological behavior and the hardened properties of cement mortars

L. Senff[a,b,*], D. Hotza[b], S. Lucas[c], V.M. Ferreira[c], J.A. Labrincha[a]

[a] Department of Ceramics and Glass Engineering, Centre for Research in Ceramics and Composite Materials (CICECO), University of Aveiro, 3810-193 Aveiro, Portugal
[b] Department of Chemical Engineering (EQA), Graduate Program on Materials Science and Engineering (PGMAT), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil
[c] Department of Civil Engineering, Centre for Research in Ceramics and Composite Materials (CICECO), University of Aveiro (UA), 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 26 May 2011
Received in revised form 29 October 2011
Accepted 31 October 2011
Available online 6 November 2011

Keywords:
Nano-silica
Nano-titania
Rheology
Flow table
Mortars
Cement

ABSTRACT

This paper reports on the use of nano-SiO_2 (nS) and nano-TiO_2 (nT) in cement pastes and mortars. Samples with 0–3 wt.% nS, 0–12 wt.% nT and 0.5 water/binder weight ratio were prepared. Rheological and flow table measurements were carried out. In addition, the design of experiments was applied to validate the results found. The temperature of hydration and compressive strength with 28 days was also determined. In general, mortars exhibited noticeable differences in the rheological behavior, but less evident in temperature of hydration and compressive strength. The values of torque, yield stress and plastic viscosity of mortars with nanoadditives increased significantly, reducing the open testing time in rheology tests. Meanwhile, the flow table values reduced. In addition, spread on table and initial yield stress exhibited a power correlation, while the spread on table and plastic viscosity did not show any special relationship. The results of kinetics of hydration followed the same tendency found by rheology, in which samples with higher amounts of nS and nT showed remarkable changes in relation to the samples without nanoadditives. Mechanical properties were not significantly affected by nanoparticles in the range considered in this work.

1. Introduction

In recent years, nanotechnology applications have been growing in different domains. Many scientific articles have been published, and within the next few years large investments will be accomplished in this area. The American National Science Foundation estimates that the annual market of components of nanotechnology will reach $ 1 trillion by 2015 [1].

In Civil Engineering, major development has been achieved through the production of materials with new functions or by improving the performance of existing ones. Such potential can already be seen today through many current applications related for instance to surface coatings, self-cleaning capacity, and fire resistance [2].

Nanoparticles have a high surface area to volume ratio. In this way, nanoparticles with 4 nm diameter have more than 50% of its atoms at the surface and are thus very reactive [3]. The behavior of such materials is mainly influenced by chemical reactions at the interface, and by the fact that they easily form agglomerates. Such agglomeration affects the rheological properties of mixtures containing nanoparticles, whose dispersion is more difficult. Moreover, the higher surface area to be wet decreases the amount of free dispersant (water in aqueous systems) available in the mixture. Therefore, the use of nanoparticles in mortars and concretes significantly modify their behavior in the fresh but also in the hardened conditions, as well as the physical/mechanical and microstructure development [4].

Several authors [5–14] have investigated the effect of nanoparticles of silica (nS) and titania (nT) in cement-based materials and, in general, they concluded that nS accelerate the chemical reactions during initial hydration [5,6]. The nS reacts with calcium hydroxide (CH) [5,7,8] and increases the amount of calcium silicate hydrate (C–S–H) produced [9], leading to a compact microstructure [7,10] and, consequently, improving the mechanical properties of hardened mixtures [5–7,10].

The major application of titanium dioxide in building materials is based on its known photocatalytic action, used for environmental pollution remediation, self-cleaning and self-disinfection [11]. If added as a bulk component to the mortar, small titania particles will reduce the amount of fine pores (<1 μm) [12]. If used as a coating layer nT apparently does not change the wear resistance of the surface [13]. In addition, the degradation rate of air pollutants

* Corresponding author at: Department of Ceramics and Glass Engineering, Centre for Research in Ceramics and Composite Materials (CICECO), University of Aveiro, 3810-193 Aveiro, Portugal. Fax: +55 48 37219687.
E-mail address: lsenff@gmail.com (L. Senff).

0921-5093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2011.10.102

by the photocatalytic layer decreases when the relative humidity increases [14].

The effect of nS and nT particles on cementitious materials has been extensively investigated [5–14]. In the latest years less common nanoparticles (Al_2O_3, Cr_2O_3, CuO, ZnO_2, ZrO_2) have been used in cementitious composites, which have been mainly characterized microstructurally and by physical and mechanical properties [15–20]. However, the use of rheology and flow table methods to define nanoparticle-added mortar formulations with suitable workability is not frequent. Particularly, the design of experiments (DOE) methodology can provide an efficient tool for those formulations.

Flow table is a common technique in civil engineering to evaluate the consistency of fresh mortars. However, it does not allow determining the consistency of mixtures for distinct deformation rates. In this way, rheometry allows measuring the rheological parameters, namely yield stress and plastic viscosity, using different deformation rates. Fresh mortar or concrete can be considered as a fluid material, where the yield stress represents the initial resistance to the flow, caused by contacts between particles, while the plastic viscosity controls the behavior once the required torque was achieved to initiate the movement [21]. The rheological behavior of mortars may be represented by the Bingham model:

$$\tau = \tau_o + \mu_p \cdot \gamma \quad (1)$$

where τ (Pa) is the shear stress, τ_o (Pa) is the yield stress, μ_p (Pa s) is the plastic viscosity and γ (s^{-1}) is the shear rate.

The Bingham model may be also expressed through torque (*T*, N mm) as a function of rotation speed (*N*, min^{-1}) by Eq. (2):

$$T = g + hN \quad (2)$$

where *g* (N mm) and *h* (N mm min) are directly proportional to the yield stress and plastic viscosity, respectively.

Design of experiments (DOE) is a methodology utilized to evaluate the effect of the main factors and their interactions on a certain property. When the interaction between two factors is significant, the impact caused by one factor is not constant and depends on the level of the other factor [22]. In this methodology, a 2^k and 3^k factorial design (*k* represents the number of factors involved, while 2 and 3 are the number of levels studied) allows adjusting the linear and quadratic regression model, respectively. Moreover, the 2^k factorial design with a central point can be used initially to check the significance of the curvature, without need to perform a full 3^k design, then reducing the number of tests. The statistical significance of this test and the validation of models may be accomplished by an analysis of variance (ANOVA) [22].

This paper reports an experimental research of the effect of nS and nT on the rheological properties of mortars, applying distinct testing times and DOE as a test methodology. In addition, temperature of hydration and compressive strength are measured in order to evaluate the performance of mixtures defined through rheometry data.

2. Experimental

2.1. Materials

Portland cement (OPC type I 42.5R), according to EN 197-1 [23] was used as a binder. It presents a specific area of 0.35 m^2/g (Blaine fineness), an average particle size of 14 μm and its chemical composition is given in Table 1. The nanosilica suspension (Levasil 200, 40 wt.%, H.C. Starck, Germany) contains 40 wt.% solids corresponding to a density of 1.3 g/cm^3; nS particles present an average size of 15 nm and specific surface area (SSA) of 200 m^2/g (BET). Nanotitania is mainly anatase (Aeroxide P25, Portugal) with specific surface area of ~50 m^2/g (BET) and an average particle size of 21 nm. The sand used as aggregate is composed by three main particle size fractions (1.2, 0.6 and 0.3 mm), each one corresponding to 33.3 wt.%, in order to improve the particle packing. The superplasticizer (SP) used to adjust the plasticity of fresh mortars is based on a polycarboxylic ester (Glenium 52, Basf, Germany), with a density of ~1.9 g/cm^3 and corresponding to 20 wt.% solids.

Table 1
Chemical composition of Portland cement CEM I – 42.5R.

Component (in wt.%)	Portland cement
SiO_2	20.37
CaO	63.05
Al_2O_3	4.78
Fe_2O_3	2.96
SO_3	3.70
MgO	2.02
Cl^-	0.018
K_2O	–
Loss on ignition	2.37

2.2. Testing procedures

The high surface area of nS and nT causes a strong impact on the mixture, restricting the maximum admissible content. The experimental plan becomes more difficult to be set, when a comparative evaluation of mortars with higher nS + nT added and REF mortar (reference mortar with nS = nT = 0%) is tried.

Two experimental plans were conducted (Table 2). In the first plan, the factorial design was used to evaluate the impact of nS (0–1.3 wt.%) and nT (0–5.2 wt.%) additions and their interactions. The maximum amount of water and SP (1.8 wt.% in relation to cement) was defined for the REF formulation. By fixing the amount of those components, nS and nT were initially added up to a maximum value, which still allowed some workability, as assessed by the rheometer. This procedure was required since the two techniques differ in relation to the minimum and maximum plasticity admissible levels. In this way, all mortars could be characterized in both equipments. REF mortar exhibits higher tendency to flow and, therefore, was defined by flow table. By contrast, mortars with nS + nT were defined by rheometry, since they are less deformable and their flow behavior is not easily fitted by the Bingham model in the initial periods.

For higher amounts of nS (2–3 wt.%) and nT (8–12 wt.%), a second plan (Table 2) was followed in which the portion of SP was adjusted according to the nanoparticles added, in order to obtain a similar

Table 2
Formulation of mortars for rheology, flow table, unrestrained shrinkage, weight variation and compressive strength.

Experimental plan	Mixture components (wt.%)			Water/binder wt. ratio	Water/solid wt. ratio
	nS	nT	SP	(W/B)	(W/S)
Plan 1	–	–	1.80	0.51	12.86
	–	2.60	1.80	0.51	12.78
	–	5.20	1.80	0.51	12.69
	0.65	–	1.80	0.51	12.84
	0.65	2.60	1.80	0.51	12.76
	0.65	5.20	1.80	0.51	12.67
	1.30	–	1.80	0.51	12.82
	1.30	2.60	1.80	0.51	12.74
	1.30	5.20	1.80	0.51	12.65
Plan 2	2.00	8.00	3.20	0.52	12.82
	2.50	10.00	4.20	0.53	12.94
	3.00	12.00	5.20	0.54	13.05
	–	1.30	1.80	0.51	12.82